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Excess Energy and Structural Dependence of the Rate of Energy Redistribution during the Photodissociation of Iodotoluenes

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Abstract

The ortho (2-), meta (3-), and para (4-) iodotoluenes (C_7H_7I) are photodissociated at 266 nm and 304 nm and studied with state-selective one-dimensional photofragment translational spectroscopy. Angular, velocity, and translational energy distributions are obtained for the ground state $I(^2P_{3/2})$ and spin-orbit excited state $I^*(^2P_{1/2})$ iodine atoms produced upon photodissociation. As has been observed in iodobenzene, the ground state I channel observed in each isomer of iodotoluene exhibits both a prompt alkyl iodide-like dissociation channel following a parallel excitation to the alkyl iodide $^3Q_0(n,\sigma^*)$ repulsive state and curve crossing to the $^1Q_1(n,\sigma^*)$ state, and a slower, indirect dissociation channel following a competitive excitation to aromatic charge transfer (π,π^*) predissociative excited states at both 266 nm and 304 nm. The I^* channel observed at both 266 nm and 304 nm for each isomer results from a prompt dissociation resulting from parallel absorption to an alkyl iodide type $^3Q_0(n,\sigma^*)$ state. The rapid I and I^* dissociative channels observed for each isomer are found to exhibit strong dependence on the excess excitation. This is discussed in terms of the increase in the density of the

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vibrational states of the toluene ring. Dissociation times and rates of internal energy redistribution (IER) from the slow dissociative channel (β) are estimated for each isomer. For 2-iodotoluene, the rate of IER for the slow I channel increases from 20 kcal/mol-ps at 304 nm to 30 kcal/mol-ps at 266 nm, while the rates of IER for 3- and 4-iodotoluene (16 kcal/mol-ps and 15 kcal/mol-ps, respectively) remain unchanged as the photon energy is increased. The difference in the observed excess energy dependence of the rates of IER in these isomers is discussed in terms of the complex coupling schemes between the optical doorway states and the n, σ^* repulsive states that produce the iodine atoms, monitored in the experiment.

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1. Introduction

The photodissociation dynamics of organic iodides have been the subject of a considerable number of spectroscopic investigations¹⁻¹⁶. It is well known that alkyl iodides photodissociate along the C-I bond when excited in the 200-300 nm region as the result of a $\sigma^* \leftarrow n$ absorption localized on the C-I bond¹⁻¹¹. The three excited states which arise from the $\sigma^* \leftarrow n$ transition are the $^3Q_1(n, \sigma^*)$, $^3Q_0(n, \sigma^*)$, and $^1Q_1(n, \sigma^*)$ states, in order of increasing energy, are all repulsive and result in the very fast formation (<0.1 ps) for methyl iodide¹¹ of photofragments with high translational energy and high spatial anisotropy. In the 200-350 nm region there are in benzene three singlet (S) and three triplet (T) (π, π^*) excited states. The singlet states are the $S_1(^1B_{2u})$, $S_2(^1B_{1u})$, and $S_3(^1E_{1u})$, with absorption maxima at approximately 255 nm, 200 nm, and 178 nm, respectively.¹⁷ The triplet states are the $T_1(^3B_{1u})$, the $T_2(^3E_{1u})$, and the $T_3(^3B_{2u})$ states, with predicted energies¹⁷ at about 320 nm, 255 nm, and 218 nm.

Aryl halides have been investigated by Bersohn and co-workers^{11,13,14} at photon excitation energies within the aromatic (π, π^*) singlet state absorption region. It was observed that photodissociation results in high internal excitation of the aromatic photofragment and reduced spatial anisotropy, relative to alkyl iodides. This has been interpreted as being due to the excitation of (π, π^*) singlet states which are predissociated by mixing with the repulsive (n, σ^*) states of the C-I bond.

Recent investigations of the photodissociation of iodobenzene at 304 nm in our laboratory¹⁵ show that ground state iodine atom is produced at this photon energy by an alkyl iodide-like $\sigma^* \leftarrow n$ transition resulting in a very fast dissociation (0.35 ps), as well as by a slow dissociation process (0.5-1.3 ps) resulting from a mixed transition. This mixed transition is believed to be due to the excitation to triplet (π, π^*) benzene type states which are predissociated by mixing the alkyl iodide (n, σ^*) states.

Information about dissociation times and energy redistribution rates were obtained by using the molecular rotation of iodobenzene as a clock¹⁵. Recent results from further investigations¹⁸ of iodobenzene at 218 nm and 266 nm suggest that the prompt dissociation process indeed results from the direct dissociation from repulsive (n,σ^*) alkyl iodide type states, while the indirect dissociation process observed at each wavelength is believed to be due to the excitation of a charge transfer (π,π^*) state. It was also found for the prompt processes that the rate of internal energy redistribution (IER) increases as the amount of excess available energy available to the system following photodissociation increases.

The substitution of an iodine atom and a methyl group for hydrogen atoms of the benzene provides an interesting system for study. In the chemistry of benzene and its derivatives both alkyl groups, such as the methyl group, and halogens, such as iodine, are ortho-para directing substituents.^{20,21} However, the inductive effect on σ electrons by the iodine atom and the methyl group are of opposite direction.²¹ The methyl group donates negative charge through the σ -bond system and activates the ortho and para sites to electrophilic substitution reactions. Conversely, iodine inductively withdraws negative charge from the ortho and para positions through the σ -bond system, deactivating these sites to electrophilic substitution. In contrast to the opposite directions of their σ inductive effects, both CH_3 and I are donors of π electrons to the benzene aromatic π system, which effectively extends the aromatic π system. This hyperconjugation of the π system, also known as the mesomeric effect, may thus affect the photodissociation dynamics of the iodotoluene isomers at 304 nm and 266 nm, since (π,π^*) states are being excited at these wavelengths.

In this work we investigate the photodissociation of ortho, meta, and para iodotoluene at 266 nm and 304 nm. The photodissociation reactions studied are



Where $\text{C}_7\text{H}_7\text{I}$ is either 2-iodotoluene, 3-iodotoluene, or 4-iodotoluene and $\text{I}(^2\text{P}_{3/2})$ is the ground state iodine atom (hereafter referred to as I) and $\text{I}(^2\text{P}_{1/2})$ is the spin-orbit excited state iodine atom (hereafter referred to as I^*). We investigate the effect the addition of the methyl substituent to iodobenzene has on the dynamics of photodissociation of the C-I bond. We observe that the dissociation dynamics are similar to iodobenzene, but we also observe differences in the nature of the slow dissociation process in 2-iodotoluene, compared to 3- and 4-iodotoluene. By using molecular rotation as a clock, we are able to estimate dissociation times and energy redistribution rates for these molecules. Differences between the dissociation dynamics are discussed in terms of the effect of the substituent positions and hyperconjugation (the mesomeric effect) on the complex coupling between the doorway π, π^* states and the n, σ^* repulsive states.

2. Experimental

Details of the experimental apparatus and methodology are described elsewhere^{10,16}. Briefly, a single-stage pulsed acceleration TOF mass spectrometer is used in combination with a linearly polarized pulsed laser (~20 ns pulsewidth). Room temperature vapor of I_2 is used to calibrate the TOF apparatus.^{10,16} At room temperature, the iodotoluene isomer (2-, 3-, or 4- $\text{C}_7\text{H}_7\text{I}$) vapor is introduced by effusion into the ionization region of the apparatus. The measured pressure is found to be about 2×10^{-6} torr.

The molecule under investigation is photolyzed by a 266 nm pulse (40 $\mu\text{J}/\text{pulse}$, the fourth harmonic frequency generated from the 1064 nm fundamental frequency), or a 304 nm pulse (30 $\mu\text{J}/\text{pulse}$, the doubled output of a pulsed dye laser pumped by the 532 nm second harmonic frequency of the 1064 nm fundamental frequency). For the two color experiment, the 266 nm photolysis pulse is spatially overlapped with the 304.02 nm or 304.67 nm ionization pulse. The ionization pulse is delayed 4 ns with respect to the photolysis pulse. The spatial overlap of the two pulses is adjusted such that the iodine ion signal is maximized. Furthermore, the photolysis and photoionization pulse energies are adjusted such that each pulse alone yields a minimized iodine ion signal. Single color background spectra are collected for each two color data file in order that the single color contribution to the two color ion signal intensity can be subtracted from the two color spectrum. Single color experiments are performed at two laser wavelengths, 304.02 nm for I^* and 304.67 nm for I , in order to selectively ionize I^* and I via 2-photon resonance plus one photon ionization following single photon dissociation within the same laser pulse. Additionally, polarizations parallel and perpendicular to the detection axis ($\alpha = 0^\circ$ and $\alpha = 90^\circ$, respectively) are used at each photolysis wavelength in order to obtain information about the angular dependences of the photodissociation processes.

A field-free condition is maintained during a delay time τ of 1.50 μs after the laser pulse. The iodine atoms are then accelerated up toward the detector by applying a pulsed acceleration voltage (approximately -1500 V with a pulse duration of 1.0 μs) to the acceleration electrode. After traveling through a field-free drift region, the ions pass through a discrimination pinhole (6.0 mm diameter) and the TOF distribution is measured. The discrimination pinhole discriminates against photoions with large velocity components perpendicular to the detection axis (velocities in the x and y directions which are greater than 120 m/s).¹⁶

3. Results

3.1. The I Photodissociation Channel at 304.67 nm

The lab. velocity distributions in the z-direction (v_z) of ground state iodine atoms produced from the photodissociation of 2-iodotoluene, 3-iodotoluene, and 4-iodotoluene at 304.67 nm are shown in figures 1(a)-(c) for laser polarization angles of $\alpha = 0^\circ$ and $\alpha = 90^\circ$ with respect to the detection axis (the z-direction). The v_z distributions are one-dimensional distributions which are obtained after discrimination against photofragments with v_{xy} greater than 120-130 m/s. Clearly, as in iodobenzene¹⁵ and 3-iodopyridine,¹⁹ there is a sharp velocity distribution and a broad velocity distribution in the v_z spectrum for each isomer.

From conservation of momentum of the photofragments, the v_z distributions are transformed into the translational energy (E_t) domain to obtain the total translational energy distribution $G(E_t)$, and the anisotropy parameter as a function of the translational energy release, $\beta(E_t)$ (figures 2(a)-(c)). One can clearly see the nature of the dependence of the spatial anisotropy on the photofragment translational energy E_t . For each isomer, in the high translational energy region, which corresponds to the sharp distribution, the value of β is high (1.6) and nearly independent of E_t . The high positive value of β in this region indicates that I is produced promptly following a parallel electronic transition. In the low translational energy region, which corresponds to the broad distribution for each isomer, the value of β clearly decreases as E_t decreases. This translational energy dependence of the anisotropy parameter indicates that energy redistribution is competing with the photodissociation process that produces the slow I on the molecular rotation time scale.

The photodissociation dynamics of the iodotoluene isomers for the 304.02 nm I* formation channel are summarized along with the results for the I formation channel in table 1. The v_z and E_t distributions are presented in figures 3(a)-(c) and 4(a)-(c), respectively, for the photodissociation of each isomer of iodotoluene at 304.02 nm. As is observed for the I* photodissociation channels of iodobenzene¹⁶ at 304.02 nm, the translational energy distribution, $G(E_t)$, for each isomer exhibits a single, relatively narrow high energy peak, in contrast to what is observed in the I channel. The observed high values of the anisotropy parameters for 2- and 3-iodotoluene ($\beta=1.5$) suggest that in these molecules, the formation of I* at 304 nm results from a prompt dissociation following an electronic absorption of parallel polarization. An interesting exception is 4-iodotoluene, which exhibits a value for the anisotropy parameter of $\beta=1.2$.

Also, in agreement with the observations of the 304 nm I* channel of iodobenzene,¹⁶ the I* relative yields (the fraction of I* produced relative to the total number of iodine atoms produced from all channels) are also quite low ($\Phi(I^*)=0.01$ for each isomer). The relative yields for I*, $\Phi(I^*)$, are calculated from

$$\Phi(I^*) = \frac{n(I^*)}{n(I^*) + n(I)} \quad (3)$$

where $n(I^*)$ is the number of I* atoms produced and $n(I)$ is the total number of slow and fast I atoms produced. The number of I or I* atoms is obtained from the integrated intensities of the appropriate $G(E_t)$ distributions. Relative yields for slow I and fast I are calculated in the same way. This relative yield is not a quantum yield because radiationless processes are not taken into account. Therefore, as in iodobenzene,¹⁶ the formation of most of the I* in 2-, 3-, and 4-iodotoluene is likely to

3.2 The I Photodissociation Channel at 266 nm

From the lab. v_z distributions presented in figures 1(d)-(f), it is clear that, as in iodobenzene¹⁸ and 3-iodopyridine,¹⁹ multiple dynamical processes are occurring during the photodissociation of each of the iodotoluene isomers at 266 nm for the I formation channel. The total translational energy distributions $G(E_t)$, and the corresponding $\beta(E_t)$, are presented in figures 2(d)-(f) for 2-, 3-, and 4-iodotoluene, respectively. As for the photodissociation process observed for each isomer at 304.67 nm, the photodissociation dynamics observed at 266 nm for each of the iodotoluene isomers result from parallel electronic transitions.

For each isomer, the observed anisotropy parameter which corresponds to the high translational energy distribution $G_h(E_t)$ is large ($\beta=1.4$ for 2- and 4-iodotoluene, $\beta=1.5$ for 3-iodotoluene) and essentially independent of the translational energy release, thus indicating that these high E_t distributions result from relatively prompt dissociations at 266 nm. However, these values for β are slightly less than the value of 1.6 obtained for each isomer at 304.67 nm, which is similar to what is observed for iodobenzene^{16,18} and 3-iodopyridine¹⁹, as the photolysis wavelength is changed from 304 nm to 266 nm. This could result from a mixed polarization nature of the absorption at 266 nm.

The anisotropy parameter observed for the low translational energy $G_l(E_t)$ distribution is dependent on E_t , indicating that this distribution arises from an indirect dissociation on the time scale of energy redistribution and molecular rotation, similar to that observed at 304.67 nm.

3.3 The I* Photodissociation Channel at 304.02 nm and 266 nm

result from an initial excitation to the alkyl iodide $^3Q_0(n,\sigma^*)$ repulsive state, which correlates with the formation of I^* in the alkyl iodides.¹⁻¹⁶

Figures 3(d)-(f) and 4(d)-(f) present for each iodotoluene isomer the lab. velocity distributions at $\alpha=0^\circ$ and $\alpha=90^\circ$, and the corresponding $G(E_t)$ and $\beta(E_t)$, respectively, for the formation of I^* following photoexcitation at 266 nm. From the values of the anisotropy parameter obtained for each isomer ($\beta=1.5$ for 2- and 4-iodotoluene, $\beta=1.7$ for 3-iodotoluene) the formation of I^* from each of the iodotoluene isomers at 266 nm results from a parallel electronic excitation followed by a prompt dissociation, in analogy with the photolysis of iodobenzene¹⁸ and 3-iodopyridine¹⁹ at 266 nm. Curve-crossing probability, not E, ought to be what affects the I^* yield. For each isomer, the I^* quantum yields increase tenfold from 0.01 at 304.02 nm to about 0.1 at 266 nm, but are still less than the value of 0.21 observed in iodobenzene at 266 nm.¹⁸ This might be due to stronger π,π^* (compared to the n,σ^* C-I) absorption in the alkyl derivatives. The latter which leads to the formation of I via a predissociation process might compete with I^* production more effectively than in iodobenzene¹⁸, thus reducing the I^* yield.

3.4 Time Dependence of the Anisotropy Parameter and the Translational Energy Release

The time dependence of the anisotropy parameter is determined for each iodotoluene isomer in order to estimate dissociation times and rates of internal energy redistribution (IER). A detailed description of the analytical methodology is provided elsewhere.¹⁶ The iodotoluene isomers are treated as symmetric top molecules after the formalism of Yang and Bersohn¹² since the two moments of inertia about the C-I bond are approximately equal. The value of the anisotropy

parameter observed at some time t , $\beta(t)$, is related to the initial value β_0 at time zero ($\beta_0=1.8$ for our experimental apparatus¹⁶) by a rotational correlation function:

$$\beta(t) = \beta_0 \langle D_{00}^2(t) \rangle \quad (4)$$

The brackets around the rotational correlation function denote an average over the rotational ensemble. This average depends on the temperature T and the asymmetry parameter $b = (I - I_z)/I_z$ where I is the perpendicular moment of inertia and I_z is the moment of inertia about the symmetric top figure axis. Figure 5 shows the rotational correlation functions as a function of reduced time t^* for each isomer. The reduced time is related to the dissociation time t by

$$t^* = t(I/kT)^{-1/2} \quad (5)$$

where the quantity $(I/kT)^{1/2}$ is the classical rotation time of the molecule. The moments of inertia and the rotation times have been calculated for each isomer and are presented in table 2. Given the rotational correlation function for each molecule, the observed values for β are used to estimate the carbon-iodine bond dissociation times, which are presented in table 1.

From the translational energy dependence of β and the dissociation time dependence of β we are able to determine the time dependences of the translational energies for the broad distributions of each isomer, and hence the rates of internal energy redistribution (IER). These observed time dependences are approximately

linear with a slope dE_t/dt of -20 kcal/mol-ps for 2-iodotoluene (figure 6(a)), -16 kcal/mol-ps for 3-iodotoluene (figure 6(b)), and -15 kcal/mol-ps for 4-iodotoluene at 304 nm (figure 6(c)). At 266 nm the rates of IER for the slow I formation channel for each isomer are found to be -30 kcal/mol-ps for 2-iodotoluene (figure 6(d)), -16 kcal/mol-ps for 3-iodotoluene (figure 6(e)), and -15 kcal/mol-ps for 4-iodotoluene (figure 6(f)).

3.5 The Partitioning of the Excess Available Energy

Upon photodissociation, there is made available to the system excess energy which is redistributed into vibrational and translational modes. The respective excess available energies for I and I*, E_{avl} and E_{avl}^* , are given by the following energy conservation relationships:

$$E_{avl} = h\nu - D_0^0(C_7H_7-I) + E_{int}^p = E_t + E_{int} \quad (6)$$

$$E_{avl}^* = E_{avl} - E_{so} = E_t^* + E_{int}^* \quad (7)$$

where $D_0^0(C_7H_7-I)$ is the dissociation energy of a ground state iodotoluene molecule into a ground state tolyl radical and an I atom at 0 K, $h\nu$ is the photolysis photon energy, E_{int}^p is the internal energy of the ground state parent molecule, E_{so} is the spin-orbit excitation energy of the iodine atom (21.7 kcal/mol), E_t and E_t^* are the translational energies of both photofragments for the I and I* channels, respectively, and E_{int} and E_{int}^* are the resulting internal energies of the tolyl radical following photodissociation into I or I* and tolyl radicals, respectively. The values of

$D_0^0(\text{C}_7\text{H}_7\text{-I})$ and $E_{\text{int}}^{\text{P}}$ are not known for these isomers and we have used the values for iodobenzene¹⁶ (63.9 kcal/mol and 2.8 kcal/mol, respectively) as an approximation.*

We find that the fractions of the excess available energy redistributed into internal energy modes for the fast I and I* channels, $\langle E_{\text{int}} \rangle / \langle E_{\text{avl}} \rangle$ and $\langle E_{\text{int}}^* \rangle / \langle E_{\text{avl}} \rangle$, increase as $\langle E_{\text{avl}} \rangle$ and $\langle E_{\text{avl}}^* \rangle$ increase, in agreement with observations made for iodobenzene¹⁸ and 3-iodopyridine¹⁹ (table 1). Furthermore, as in the cases of iodobenzene¹⁸ and 3-iodopyridine,¹⁹ the full widths at half maximum (FWHM's) of both the fast I and I* translational energy distributions of each isomer of iodotoluene increase as the excess available energy increases. These observations indicate that the redistribution rate of the excess available energy via the prompt I and I* channels becomes faster with increasing the excess available energies. Finally, we observe for each isomer of iodotoluene that the total internal energy exhibits a strong photon energy dependence (figure 7), in accordance with observations made for iodobenzene,¹⁸ 3-iodopyridine,¹⁹ and CF_3I ,^{5,16,22} indicating that tolyl vibronic levels are strongly coupled to the carbon-iodine dissociative optical doorway state.

4. Discussion

4.1 The Dynamics of Photodissociation at 266 nm and 304 nm: the Fast I Channel

As was observed for iodobenzene¹⁵, the ortho, meta, and para isomers of iodotoluene exhibit at least two distinct photofragment speed distributions for the I channel at 304 nm and 266 nm. Undoubtedly, the high speed, and thus high translational energy distributions, are due to the prompt dissociation of the C-I bond

* * For the iodotoluene isomers the value of $E_{\text{int}}^{\text{P}}$ is likely to be greater than the value of 2.8 kcal/mol reported for iodobenzene due to the presence of the additional methyl group internal energy modes. This could increase E_{avl} and E_{int} , possibly resulting in an increase in the fraction of excess available energy partitioned into internal energy modes.

as a result of excitation of a predominantly localized $\sigma^* \leftarrow n$ transition. This is evidenced by the high values of the anisotropy parameters (1.6 for each isomer at 304 nm, 1.4-1.5 at 266 nm, see table 1), and hence fast dissociation times (~ 0.4 ps at 304 nm for each isomer, 0.5-0.6 ps at 266 nm for each isomer) which is similar to what is observed in iodobenzene¹⁸ and 3-iodopyridine.¹⁹

As is observed in iodobenzene¹⁸ and 3-iodopyridine,¹⁹ the value of the anisotropy parameter decreases in magnitude as the excitation wavelength is changed from 304 nm to 266 nm. This might indicate that the excited state which leads to the formation of fast I photofragments from each isomer of iodotoluene, although repulsive, interacts with the benzene type bound states. This is not surprising if one considers the mesomeric effect,²¹ which causes a conjugated π -electron system to be effectively extended, or hyperconjugated, by a substituent (or substituents) which donates electron density to the conjugated system. Iodine and the methyl group are well known to be strongly mesomeric substituents²¹; the methyl group donates electron density from its sp^3 orbitals, and the iodine atom donates electron density from its p_π non-bonding orbitals. In aromatic iodides, such as iodobenzene or the iodotoluenes, in addition to the carbon-iodine (n, σ^*) alkyl iodide states, singlet and triplet charge transfer (π, π^*) bound states are formed along the carbon-iodine bond due to the mixing of iodine p_π and aromatic π -electrons, with these charge transfer states polarized along the carbon-iodine bond axis. Thus it should be expected that the excited state which produces fast I, which is likely an alkyl iodide (n, σ^*) repulsive state, becomes strongly coupled to a benzene (π, π^*) bound state(s) due to the mesomeric effect. As the excitation energy increases, the density of ring and methyl group vibrational states increase. This increases the rate of energy redistribution into these modes as the rate is given by:

$$\text{Rate} = \rho/\hbar \langle \Psi_{n,\sigma^*} | \Psi_{\pi,\pi^*} \rangle^2, \quad (8)$$

where ρ is the density of the π,π^* vibronic states at the n,σ^* excitation energy, and $\langle \Psi_{n,\sigma^*} | \Psi_{\pi,\pi^*} \rangle$ is the electronic matrix element coupling the two different electronic states.

It is also quite possible that polarization of the $\sigma^* \leftarrow n$ transition is a mixture of parallel and perpendicular polarization components. Such mixed transitions have been observed in the alkyl iodides, and it has been shown that the relative contributions of the 3Q_0 , 3Q_1 and 1Q_1 states to the A-band absorption intensity depend on the type of alkyl group.²⁴ It would not be unreasonable to expect the phenyl group to affect the relative contributions of these (n,σ^*) states to the carbon-iodine absorption. The value of β for a mixed transition which results in a prompt dissociation can be expressed as a sum of the relative contributions of the parallel and perpendicular transitions:^{4,17}

$$\beta = x_{\parallel} \beta_{\parallel} + x_{\perp} \beta_{\perp} \quad (9)$$

where β_{\parallel} and β_{\perp} are the limiting values of the anisotropy parameters for parallel and perpendicular transitions, respectively, and x_{\parallel} and $x_{\perp} = (1 - x_{\parallel})$ are fractional contributions of β_{\parallel} and β_{\perp} to β , respectively. It has been shown that for our apparatus, due to various apparatus depolarization effects, the limiting values of β ^{10,15,16} are $\beta_{\parallel} = 1.63$ and $\beta_{\perp} = -0.8$. Therefore the slightly lower values of β observed here at 266 nm may also be due to less than 10% contribution of a perpendicular component due to a transition to the 1Q_1 state.

At 304 nm, the benzene (π, π^*) states which are available for mixing with alkyl iodide (n, σ^*) states are triplets (the 3L_a and 3L_b). Thus it is proposed for the photolysis of the iodotoluene isomers at 304 nm that the fast I channel arises from excitation to the of $^3Q_0(n, \sigma^*)$ optical doorway repulsive state, followed by crossing to the $^1Q_1(n, \sigma^*)$ exit state. At 266 nm, the benzene type bound state which is available for mixing with alkyl iodide repulsive states is the $^1L_b(\pi, \pi^*)$ state (which is of perpendicular polarization). The fact that the transition observed at 266 nm is parallel suggests that the fast I channel observed for each isomer of iodotoluene also arises from excitation to the alkyl iodide $^3Q_0(n, \sigma^*)$ optical doorway repulsive state, followed by crossing to the $^1Q_1(n, \sigma^*)$ state. The observed slight decrease in the value of the anisotropy parameter on going from 304 nm to 266 nm for the fast I channel observed for each isomer might indicate that the doorway state excited at 266 nm becomes more strongly coupled to the benzene type vibronic dark states than when it is excited at 304 nm.

It is instructive to examine the photon energy dependence of the internal energy of the tolyl radicals following photodissociation of 2-, 3-, or 4-iodotoluene (figure 7). As with iodobenzene,¹⁸ the internal energy of the tolyl radical produced from each isomer is strongly dependent on the photon energy, in close analogy with the photon energy dependence of the internal energy of CF_3 following the photodissociation of CF_3I .^{5,16,22} In CF_3I , this strong photon energy dependence is interpreted as indicating that the CF_3 umbrella mode becomes strongly coupled to the dissociation along the carbon-iodine dissociation coordinate^{5,16,22} as the excess energy (or photon energy) increases. Therefore, as has been proposed for iodobenzene¹⁸ and 3-iodopyridine¹⁹ in analogy with CF_3I ,^{5,16,22} the strong photon energy dependence of the internal energy of the tolyl radicals indicates that vibronic levels of the tolyl radicals which are dark states, become increasingly

strongly coupled to the carbon-iodine $^1Q_0(n,\sigma^*)$ dissociative optical doorway state as the photon energy and thus excess energy is increased.

4.2 The Dynamics of Photodissociation at 266 nm and 304 nm: the I^* Channel

In general, the I^* channels observed for each isomer at 266 nm and 304 nm correspond to parallel transitions which give values of β that are large (1.5-1.7), and in each case are undoubtedly due an excitation to and prompt dissociation from the repulsive $^3Q_0(n,\sigma^*)$ alkyl iodide state. This is in accord with what is observed for iodobenzene^{16,18} and 3-iodopyridine.¹⁹ A notable exception is the I^* channel observed for 4-iodotoluene at 304 nm, in which the anisotropy parameter is observed to be surprisingly low ($\beta=1.2$) while at 266 nm the value of the anisotropy parameter ($\beta=1.5$) is in accordance with those determined for the ortho and para isomers. The reasons for this anomaly at 304 nm are not clear. The fact that the anisotropy parameter for the 4-iodotoluene I^* channel is essentially independent of the translational energy release suggests that the dissociation is from a repulsive state (the $^3Q_0(n,\sigma^*)$ state). A possible explanation is that because the methyl group is aligned with the carbon-iodine dissociation coordinate, its internal rotational and vibrational modes may cause significantly more distortions of the molecule than if the methyl group was positioned ortho or meta to the iodine atom. Such a distortion could then result in depolarization which gives the anomalously low value of β observed for 4-iodotoluene at 304 nm. Another possibility could be that rapid production of I^* could result in this molecule from absorption to a π,π^* state. Mixed or perpendicular polarization of absorption to the latter state could reduce the observed β .

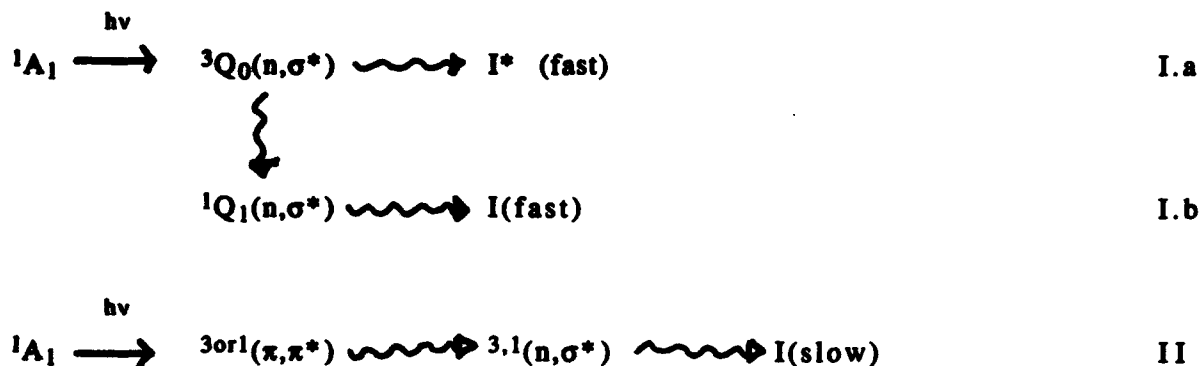
From figure 7, it is clear that the internal energy of the I* channel for each isomer is strongly photon energy dependent, indicating that observed I* channels for the iodotoluene isomers produce tolyl radicals which gain much internal excitation due to the coupling of tolyl dark vibronic levels to the carbon-iodine $^3Q_0(n,\sigma^*)$ optical doorway state.

4.3. The Dynamics of Photodissociation at 266 nm and 304 nm: the Slow I Channel

The broad distributions observed at 266 nm and 304 nm for each isomer, as in iodobenzene,^{16,18} are likely due to the excitation of benzene type singlet or triplet (π,π^*) bound states which are strongly mixed with the singlet or triplet iodobenzene charge transfer (π,π^*) states which arise from mixing with iodine electrons. This accounts for the observed parallel polarization of the electronic transition observed at 266 nm, since a pure 1L_b state in monosubstituted benzene is expected to be polarized perpendicular to the carbon-iodine bond axis. The charge transfer state is polarized parallel to the carbon-iodine bond axis, which gives the resulting parallel transition observed for the slow I distribution at 266 nm. For the photodissociation of iodobenzene at 304 nm it was proposed¹⁶ that the slow I channel resulted from a parallel absorption to either the iodobenzene $^3L_a(\pi,\pi^*)$ or $^3L_b(\pi,\pi^*)$ states followed by predissociation by the repulsive alkyl iodide $^3Q_0(n,\sigma^*)$ state to give slow I. Undoubtedly the pure benzene $^3L_a(\pi,\pi^*)$ and $^3L_b(\pi,\pi^*)$ states will mix with triplet (π,π^*) charge transfer states of iodobenzene to give the observed parallel transition, regardless of the polarizations of the pure benzene states. Thus, for photoexcitations of the iodotoluene isomers at 304 nm and 266 nm, as has been proposed for iodobenzene,^{16,18} the (π,π^*) excited state of a given iodotoluene isomer is likely predissociated by mixing with the repulsive (n,σ^*) alkyl iodide type state(s), giving dissociation times longer than those observed for dissociations from the pure (n,σ^*)

states but much faster than from pure benzene type states. This, coupled with the fact that the tolyl group has a large number of internal degrees of freedom, allows efficient energy redistribution resulting in broad translational energy distributions with relatively low average translational energies.

For the photodissociation of the isomers of iodotoluene at 266 nm and 304 nm, a general photodissociation mechanism scheme, like those proposed for iodobenzene^{16,18} and 3-iodopyridine,¹⁹ is proposed:



4.4 The Rates of Internal Energy Redistribution in the Slow (Predissociative) Channel

The time dependences of the translational energy releases of the three isomers are given in table 1. These values, dE_t/dt , are the slopes obtained from the translational energy vs. dissociation time plots in presented in figure 6. These time dependences, first reported for iodobenzene,^{15,16(a)} reflect the rates of the internal energy redistribution (IER) of the excess available energy following light absorption to the predissociative (π,π^*) states that leads to the production of slow I for these isomers. At 304 nm, the rate of IER observed for the slow I channel is largest in 2-iodotoluene (20 kcal/mol-ps), which is about 5 kcal/mol-ps larger than those rates observed for 3-iodotoluene (16 kcal/mol-ps) and 4-iodotoluene (15 kcal/mol-ps). A similar trend is observed for the slow I distributions observed in these molecules at 266 nm (30

kcal/mol-ps for 2-iodotoluene, 16 kcal/mol-ps for 3-iodotoluene, and 15 kcal/mol-ps for 4-iodotoluene).

It might be expected that the iodotoluene isomers should have higher IER rates than that for iodobenzene (23 kcal/mol ps¹⁵) due to the presence of the additional methyl internal modes. However, with the exception of 2-iodotoluene at 266 nm, just the opposite is observed. Another observation that suggests that the density of states alone is not the major factor that influences the rate of energy redistribution is the excess energy dependences of these rates. The rates of IER for the slow I channels of 3- and 4-iodotoluene are virtually identical at 266 nm and 304 nm while that for 2-iodotoluene is considerably larger at each wavelength. Furthermore, the rate of IER for the slow channel of 2-iodotoluene increases from 20 kcal/mol-ps to 30 kcal/mol-ps as the excess available energy is increased, while those for the other isomers remain unchanged as the photon energy is changed.

The above results supports our previous conclusions reached from the study of the excess energy dependence of the rate of IER in the predissociative channel in iodobenzene.¹⁸ The factors that determine the rate of energy redistribution as measured from the translation energy release of the iodine atom are more complex than those involved in the prompt channel. The reason for this is the fact that while the optical doorway state and the state that produces the iodine atoms are the same (the n,σ^* state) in the prompt channel, they are not the same in the slow channel. In the latter, the optical doorway state is the π,π^* state. Mixing of the optical doorway state with the dark π,π^* vibronic states leads to energy redistribution into the ring and methyl modes. This mixing indeed increases as the excess energy (or excitation frequency) increases. Some of these mixed dark π,π^* levels, but not all, can mix with the n,σ^* repulsive surface to produce the iodine atom that we detect in our experiment. Thus the expression for the rate of energy redistribution in the

slow channel contains, in addition to the density of the dark π,π^* states, two different electronic matrix elements: one involving the (π,π^*) states themselves and the other involving some of the π,π^* states and the repulsive n,σ^* states. These electronic matrix elements would be sensitive to the electronic structure in the vicinity of the vibronic states being excited by the photolysis laser pulse.

The presence of the methyl group might shift the predissociated (π,π^*) state(s) in energy relative to the (n,σ^*) state(s) such that both matrix elements between the π,π^* states as well as that between π,π^* and σ,π^* states change. This could lead to the observed reduction of the rate of IER relative to iodobenzene. The methyl group may also increase the coupling between some of the dark, bound π,π^* states and the repulsive n,σ^* states not far in energy from the optical excitation energies, causing the predissociation process to become more efficient than the rate of energy redistribution between π,π^* states, and thus result in the lowering of the rate of IER.

For the case of 2-iodotoluene, it is not surprising that the rate of IER increases as the excess available energy increases due to the close proximity of the methyl group to the iodine atom. One possible reason for the observed increase with photon energy of the rate of IER in 2-iodotoluene may be due to hyperconjugation of the aromatic π -electron system from the iodine atom to the methyl group. Excitation of the charge transfer 3 or $^1(\pi,\pi^*)$ state, which is polarized along the C-I bond and vibronically coupled to singlet or triplet benzene type (π,π^*) state, will cause vibrational excitation of the carbon-methyl bond through the hyperconjugative system. In this manner the excess available energy can be redistributed into internal energy modes of the methyl group. The observation that the rates of IER are essentially identical in 3- and 4-iodotoluene is also consistent with the hyperconjugation picture. As discussed earlier, theoretical simulations by Mulliken²⁴ on toluene indicate that the negative charge density is greatest at the

ortho position. This allows for stronger coupling between the π,π^* states and the C-I states if the iodine is in the ortho rather than in the meta or para positions with respect to the methyl group.

In conclusion it is observed that the overall photodissociation dynamics observed for the isomers of iodotoluene are much like those observed in the photodissociation of iodobenzene^{16,18} and 3-iodopyridine¹⁹ at 266 nm and 304 nm. They result from two competitive channels resulting from absorptions to two different excited states. One is to a charge transfer (π,π^*) state (which is vibronically mixed with a benzene-type (π,π^*) state that is predissociated by mixing with an alkyl iodide (n,σ^*) repulsive states) and the other is to an alkyl iodide type $^3Q_0(n,\sigma^*)$ repulsive state which is strongly coupled to a benzene (π,π^*) state(s). The first absorption gives rise to the slow iodines while the latter one produces the fast iodines. The fast I and I* channels observed for each isomer are found to exhibit a strong photon energy dependence of the internal energy of the tolyl radical, indicating that there is a strong coupling between the toluene vibrational modes and the carbon-iodine dissociative doorway state. The rate of IER for the slow I channel of 2-iodotoluene is found to increase with the photon energy, while for 3- and 4-iodotoluene the respective rates of IER remain unchanged as the photon energy is increased. This is explained by the complex nature of the matrix elements involved in the rate of IER as detected from the translation energy spectra of the iodine while exciting π,π^* type states.

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Figure 1

Lab. velocity distributions of the iodine ions in the z-direction for the $I(^2P_{3/2})$ channel formed from the photodissociation of (a) 2-iodotoluene, (b) 3-iodotoluene, and (c) 4-iodotoluene at 304.67 nm; (d) 2-iodotoluene, (e) 3-iodotoluene, and (f) 4-iodotoluene at 266 nm. The upper trace in each figure is for photolysis with parallel polarized light, and the lower trace is for photolysis with perpendicular polarized light.

Figure 2

The high and low total translational energy distributions, $G_h(E_t)$ and $G_l(E_t)$, and the corresponding $\beta_h(E_t)$ and $\beta_l(E_t)$, for the I photodissociation channel of (a) 2-iodotoluene, (b) 3-iodotoluene, and (c) 4-iodotoluene at 304.67 nm; (d) 2-iodotoluene, (e) 3-iodotoluene, and (f) 4-iodotoluene at 266 nm. In each case $\beta_h(E_t)$ is independent of the translational energy while $\beta_l(E_t)$ decreases smoothly as E_t decreases.

Figure 3

Lab. velocity distributions in the z-direction for the iodine fragments formed from the $I^*(^2P_{1/2})$ channel following photodissociation of (a) 2-iodotoluene, (b) 3-iodotoluene, and (c) 4-iodotoluene at 304.02 nm; (d) 2-iodotoluene, (e) 3-iodotoluene, and (f) 4-iodotoluene at 266 nm. The upper trace in each figure is for photolysis with parallel polarized light, and the lower trace is for perpendicular polarized light.

Figure 4

Total translational energy release distributions $G(E_t)$ and the anisotropy parameters as a function of translational energy, $\beta(E_t)$, for the I^* photodissociation channel of (a) 2-iodotoluene, (b) 3-iodotoluene, and (c) 4-iodotoluene at 304.02 nm; (d) 2-iodotoluene, (e) 3-iodotoluene, and (f) 4-iodotoluene at 266 nm.

Figure 5

Rotational correlation functions for (a) 2-iodotoluene, (b) 3-iodotoluene, and (c) 4-iodotoluene as functions of reduced time, t^* . The reduced time is the dissociation time, t , divided by the molecular rotational time, t/t_r . The rotational times are $t_r = 1.77$ ps, 1.96 ps, and 2.08 ps at 298 K for 2-, 3-, and 4-iodotoluene, respectively.

Figure 6

Total translational energy release as a function of time for the low translational energy distribution of the I channel resulting from the photodissociation of (a) 2-iodotoluene, (b) 3-iodotoluene, and (c) 4-iodotoluene at 304.67 nm; and (d) 2-iodotoluene, (e) 3-iodotoluene, and (f) 4-iodotoluene 266 nm. The slopes, dE_t/dt , represent the rates of internal energy redistribution following excitation. These rates are found to be: for 2-iodotoluene -20 kcal/mol-ps at 304.67 nm and -30 kcal/mol-ps at 266 nm; for 3-iodotoluene ~16 kcal/mol-ps at 304.67 nm and 266 nm; for 4-iodotoluene -15 kcal/mol-ps at 304.67 nm and 266 nm; compared with the value of -23 kcal/mol-ps reported in reference 16 for the

photodissociation of iodobenzene at 304.67 nm and to the value of -15 kcal/mol-ps reported in reference 18 for the photodissociation of iodobenzene at 266 nm.

Figure 7

Plot of the photon energy dependence of the internal energy of the tolyl radicals following photodissociation of (a) 2-iodotoluene, (b) 3-iodotoluene, and (c) 4-iodotoluene at 266 nm and 304 nm, and for comparison, (d) internal energy of the CF_3 radical following the photodissociation of CF_3I at 248 nm and 304 nm. The internal energies for the CF_3 radical at 304 nm are taken from reference 16, while the internal energy of the CF_3 radical at 248 nm is taken from reference 22. The solid circles are for the fast I channel, and the open circles are for the I^* channel. The strong photon energy dependence of the internal energy of the tolyl radical produced from each isomer of iodotoluene indicates that, in analogy with the photodissociation of CF_3I , the dark vibronic states of the tolyl radical are strongly coupled to the $^3\text{Q}_0(\text{n},\sigma^*)$ optical doorway state during the prompt dissociation process.

Table 2: Moments of inertia and rotational times calculated for the iodotoluene series and iodobenzene.

Molecule	I_A	I_B	I_C	I	b	$t_{rot}(ps)$
2-C ₇ H ₇ I	28.9	113.9	142.8	128.4	3.4	1.77
3-C ₇ H ₇ I	25.5	145.2	170.7	158.0	5.2	1.96
4-C ₇ H ₇ I	14.7	169.9	184.6	177.3	11.1	2.08
C ₆ H ₅ I	14.7	112.7	127.4	120.0	7.2	1.70
C ₆ H ₅ I ^a	14.8	111.8	126.6	119.2	7.05	1.70

^a From reference 11.

Moments of inertia are in units of 10^{-39} g-cm². $I_A = I_z$.

$I = (I_B + I_C)/2$

